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# Determination of the molecular diffusion coefficients in ternary mixtures by the Sliding Symmetric Tubes technique

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A new analytical methodology has been developed to determine the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures by the Sliding Symmetric Tubes technique. The analytical solution is tested in binary mixtures obtaining good agreement with the results of the literature. Results are presented for the ternary mixture formed by tetralin, isobutylbenzene and dodecane with an equal mass fraction for all the components (1-1-1) which is held at 25°C. Diagonal and cross-diagonal coefficients are determined for the three possible orders of components, in order to compare the results with those available in the literature. A comparison with published results shows a good agreement for the eigenvalues of the diffusion matrix, and a reasonable agreement for the diagonal molecular diffusion coefficients.

## I. INTRODUCTION

The phenomenon of molecular diffusion in multicomponent mixtures has attracted a great interest within the scientific community, and it has been analyzed in multiple processes of different sectors, such as human biology (Ref. 1), materials engineering (Ref. 2) or food industry (Ref. 3).

In 1855 Fick established the first quantitative relation for molecular diffusion, known as Fick's law (Ref. 4), and since then different experimental procedures have been developed in order to determine the molecular diffusion coefficient. In the case of binary mixtures this phenomenon has been studied in depth and currently there are many well-established and proven experimental techniques which allow the determination of this coefficient. Among them are Thermal Diffusion Forced Rayleigh Scattering (TDFRS) (Ref. 5), Open Ended Capillary (OEC) (Ref. 6), Optical Beam Deflection (Ref. 7), Optical Digital Interferometry (Ref. 7), techniques that use the Taylor dispersion principle (Ref. 8) and the Sliding Symmetric Tubes (SST) technique (Ref. 9).

In the case of ternary mixtures, the existence of diagonal and cross-diagonal molecular diffusion coefficients makes their determination considerably more difficult. In the last few years several works have been published in which the determination of these molecular diffusion coefficients has been attempted; however, the availability of results in the literature is limited, so currently, the reliability of these methods has still to be tested. For example, Königer *et al.*<sup>10</sup> tried to solve the problem applying a second wavelength for the determination by the Two Colour Optical Beam Deflection technique; Mialdun *et al.*<sup>11</sup> devised a new instrument based on interferometry to determine the molecular diffusion coefficients. Leahy-Dios *et al.*<sup>12</sup> used the OEC technique combining the density and refractive index measurements for the determination of the molecular diffusion coefficients and Santos *et al.*<sup>13</sup> and Capuano *et al.*<sup>1</sup> used the Taylor dispersion principle and the Gouy interferometer respectively. In addition, simulations based on molecular dynamics (Ref. 14) and prediction models (Ref. 3) have been undertaken in order to determine the molecular diffusion coefficients in ternary mixtures. In Larrañaga *et al.*<sup>15</sup> an analytical solution applied to SST technique was developed to determine the diffusion coefficients in ternary mixtures. Recently, Mialdun *et al.*<sup>16</sup> have published a new paper determining the molecular diffusion coefficients in ternary mixtures by two independent experimental techniques: Taylor dispersion technique and digital interferometry applied to a Counter Flow Cell.

As commented in Mialdun and Shevtsova<sup>17</sup>, the correct determination of the molecular diffusion coefficients is very important for the determination of the thermodiffusion coefficients because, except in the case of the thermogravitational column, in the other techniques it is

necessary to consider these two diffusion coefficients combined with Soret coefficient, so that the thermodiffusion coefficient for each component may be determined.

Therefore, the principal objective of the present work is the determination of the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures by the SST technique. To this end, the mixture formed by 1,2,3,4-tetrahydronaphthalene (THN), isobutylbenzene (IBB) and n-dodecane (nC12), with equal mass fraction and at 25°C has been used. This mixture was selected by the group which takes part in the project DCMIX (Ref. 18) and which is formed by 14 teams at international level in order to perform analytical, numerical and experimental studies both in terrestrial conditions and in microgravity, by the installation Selectable Optical Diagnostic Instrument (SODI) in the International Space Station and by applying a purely optical analysis system based on two wavelengths.

This article is organized as follows: in section II the methodology, both experimental and analytical, for the determination of the molecular diffusion coefficients by the SST technique is described. In section III, experimental results obtained for both binary and ternary mixtures and the discussion about them are presented. Finally, conclusions are given in section IV.

## **II. METHODOLOGY**

### **A. Experimental procedure**

The SST technique has been successfully applied in the case of binary mixtures (Refs. 19-21) and it consists of several sets of tubes (Figure 1) which have two positions. In the faced tubes position, the contents of both tubes are in contact and the transport of matter between the tubes arises by molecular diffusion. By contrast, in the separated tubes position the diffusive process is stopped. All the tubes are filled with the same mixture, but with a slight difference of concentration between the upper and bottom tubes. In an experiment, all the sets of tubes are filled in the separated tubes position and they are introduced into a water bath (see Figure 2) with a temperature control of 0.1 °C, which will maintain them at the same temperature throughout the whole experiment. At the beginning of the experiment all the sets are changed to the faced tubes position so that diffusion may be initiated. From that moment, at various predetermined intervals of time, each tube is changed to the separated tubes position, to preserve their contents for later

analysis. At the end of the experiment, the variation of the concentration with time is constructed from the concentrations in each of the tubes (see Figure 3).

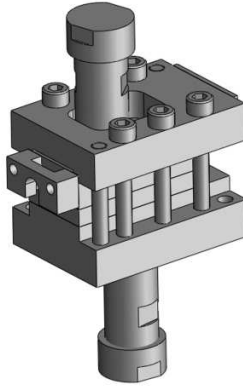


FIG. 1. A set of Sliding Symmetric Tubes.

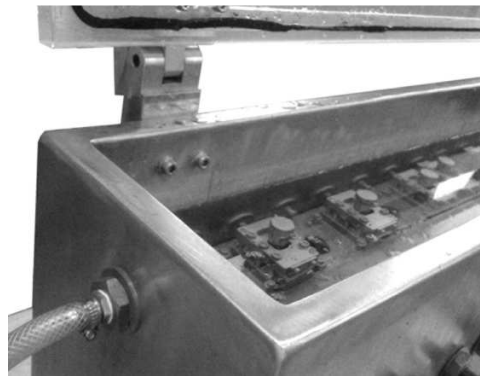


FIG. 2. Installation of the Sliding Symmetric Tubes technique.

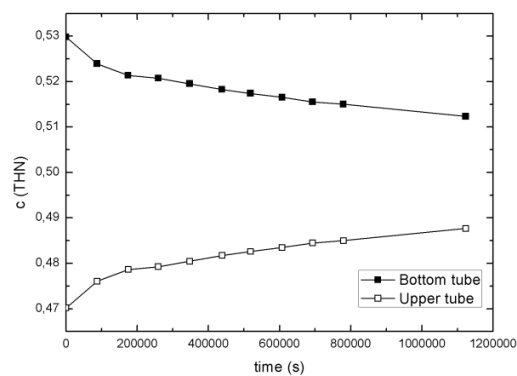


FIG. 3. Variation of the concentration with time in the upper and the bottom tubes determined by the SST technique, for the mixture THN-IBB with 50% mass fraction and at 25°C.

In order to determine the concentration of each point in a ternary mixture, its density and refractive index are measured by an Anton Paar DMA 5000 vibrating quartz U-tube densimeter with an accuracy of  $5 \times 10^{-6} \text{ g/cm}^3$  and by an Anton Paar RXA 156 refractometer with an accuracy of  $2 \times 10^{-5} \text{ RIU}$ , respectively. Mialdun and Shevtsova<sup>17</sup> and Sawicka and Soroka<sup>22</sup> show that these two properties allow the most accurate determination of the concentration of each component. In order to determine the concentration from the density and the refractive index it is necessary to do a prior calibration where measurements are made of the density and the refractive index of 25 mixtures with concentrations that are close to that of the study. Once the calibration coefficients are determined, the concentration of each component,  $w_i$ , in each point is calculated by the following equations:

$$w_1 = \frac{c'(\rho - a) - c(n_D - a')}{bc' - b'c}, \quad (1)$$

$$w_2 = \frac{b(n_D - a') - b'(\rho - a)}{bc' - b'c}, \quad (2)$$

$$w_3 = 1 - w_1 - w_2, \quad (3)$$

where  $\rho$  and  $n_D$  are the density and the refractive index respectively, and  $a, a', b, b', c$  and  $c'$  are the calibration parameters calculated for the mixture (see Larrañaga *et al.*<sup>15</sup> for details).

## B. Analytical solution

First, an analytical solution for binary mixtures was developed, which allowed the determination of the molecular diffusion coefficient from the experimental measurements of the variation of the concentration with time (Ref. 19). The working equations are the following:

$$\begin{aligned} w^{bot}|_m(t) &= \frac{w_i^{bot} + w_i^{up}}{2} \\ &= \frac{4}{\pi^2} \cdot (w_i^{bot} - w_i^{up}) \cdot \sum_{n=0}^{\infty} \frac{e^{-\left(n+\frac{1}{2}\right)^2 \frac{\pi^2}{L^2} D \cdot t}}{(2n+1)^2}, \end{aligned} \quad (4)$$

$$\begin{aligned} w^{up}|_m(t) &= \frac{w_i^{bot} + w_i^{up}}{2} \\ &= \frac{4}{\pi^2} \cdot (w_i^{up} - w_i^{bot}) \cdot \sum_{n=0}^{\infty} \frac{e^{-\left(n+\frac{1}{2}\right)^2 \frac{\pi^2}{L^2} D \cdot t}}{(2n+1)^2}, \end{aligned} \quad (5)$$

where  $w^{up}|_m(t)$  and  $w^{bot}|_m(t)$  are the mean concentration in the upper and lower tubes respectively, as functions of time;  $w_i^{up}$  and  $w_i^{bot}$  are the respective initial concentrations,  $D$  is the molecular diffusion coefficient, which is constant in the case of small concentration variations, and  $L$  is the length of the tube.

As may be noted, the formulae given in Eqs. (4) and (5) are linearly dependent and therefore it follows, not surprisingly, that the molecular diffusion coefficient must be the same in both tubes for binary mixtures.

In Larrañaga *et al.*<sup>15</sup> an initial analytical solution for ternary mixtures was obtained by following the same Fourier series procedure as for the case of binary mixtures. The evolution of the mean concentration of component  $j$  was found to take the following form:

$$\begin{aligned} \phi_j^{bot}|_m(t) - \frac{\phi_{ji}^{bot} + \phi_{ji}^{up}}{2} \\ = \frac{4}{\pi^2} \cdot (\phi_{ji}^{bot} - \phi_{ji}^{up}) \cdot \sum_{n=0}^{\infty} \frac{e^{-\left(n+\frac{1}{2}\right)^2 \frac{\pi^2}{L^2} \lambda_j \cdot t}}{(2n+1)^2}, \end{aligned} \quad (6)$$

$$\begin{aligned} \phi_j^{up}|_m(t) - \frac{\phi_{ji}^{bot} + \phi_{ji}^{up}}{2} \\ = \frac{4}{\pi^2} \cdot (\phi_{ji}^{up} - \phi_{ji}^{bot}) \cdot \sum_{n=0}^{\infty} \frac{e^{-\left(n+\frac{1}{2}\right)^2 \frac{\pi^2}{L^2} \lambda_j \cdot t}}{(2n+1)^2}, \end{aligned} \quad (7)$$

for  $j=1, 2$  and where  $\phi_j^{up/bot}|_m(t)$  is the new variable for the mean concentration in the upper and the lower tubes respectively,  $\phi_{ji}^{up/bot}$  is the new variable for the initial concentration in the upper and the lower tubes respectively and the  $\lambda_j$ -values are the eigenvalues of the diffusion matrix.

As may be observed, these equations have now become considerably more complicated and in this case there are two linearly independent equations (for each components 1 and 2) with four unknowns (the two diagonal diffusion coefficients and another two cross-diagonal diffusion coefficients). That is why a non-linear fitting had to be applied in order to determine the diffusion coefficients. Before applying the fitting, the changes of variable were undone, so that the equations became more complicated but we could fit directly the four diffusion coefficients.

However, the complexity of the equations made it impossible to achieve reliable results with different fitting methods, as is detailed in Larrañaga *et al.*<sup>15</sup>.

That difficulty has motivated the development of a new analytical solution which allows the determination of the diffusion coefficients for both binary and ternary mixtures. The new analytical solution is based on the well-known self-similar solution of Fourier's equation for an impulsively heated solid which is found in Carslaw and Jaeger<sup>23</sup>, and it is described hereafter; the method is illustrated first for binary mixtures and then it is extended to ternary mixtures.

### 1. New analytical solution for binary mixtures

It is intended to solve Fick's second law,

$$\frac{\partial w}{\partial t} = D \cdot \frac{\partial^2 w}{\partial y^2}, \quad (8)$$

for relatively short times, by which we mean that the developing interface between the upper and lower tubes has not yet reached the far ends of those tubes. In this regime the evolving front satisfies a self-similar solution for which the following changes of variable are required:

$$\eta = \frac{y}{2\sqrt{Dt}}, \quad (9)$$

$$\tau = \sqrt{t}, \quad (10)$$

where  $y$  is the vertical variable. Whilst within the self-similar regime the time-derivative may be neglected and therefore the equation for the concentration transforms to:

$$w'' + 2\eta w' = 0, \quad (11)$$

where  $w'$  and  $w''$  are the first and the second derivatives of the concentration with respect to  $\eta$ .

The boundary conditions in this case, taking into account the variable transformation, are the following:

$$\begin{aligned} w &\rightarrow w_i^{bot} \text{ as } \eta \rightarrow -\infty, \\ w &\rightarrow w_i^{up} \text{ as } \eta \rightarrow +\infty, \end{aligned} \quad (12)$$

where  $w_i^{up}$  and  $w_i^{bot}$  are the initial concentration in the upper and lower tubes respectively. Upon solving the equation (11) the following expression for the concentration is obtained:



$$w = w_i^{up} + \frac{w_i^{bot} - w_i^{up}}{2} \operatorname{erfc}(\eta), \quad (13)$$

where  $\operatorname{erfc}(\eta)$  is the well-known complementary error function of  $\eta$  (Ref. 23).

The mean concentration in each tube is obtained by integrating the solution given in the equation (13) over the length of the tube, and then dividing it by the length of the tube,  $L$ .

$$\frac{1}{L} \int_0^L w \, dy = w_i^{up} + \frac{(w_i^{bot} - w_i^{up})}{L} \sqrt{\frac{Dt}{\pi}}. \quad (14)$$

It is important to note that Equation (14) remains valid until the diffusion front (i.e. the region of mixing between the two reservoirs) begins to reach the ends of the tubes. Equation (14) shows that the mean concentration varies linearly with  $t^{1/2}$  and therefore Figure 4 has been created to show this linear variation of the upper and lower mean concentrations with the square root of time for the mixture THN-IBB with mass fraction of 50% and at 25°C. As can be seen, the variations are almost linear and therefore the molecular diffusion coefficient as given by the upper tube data may be determined directly by the following expression:

$$S^{up} = \frac{(w_i^{bot} - w_i^{up})}{L} \sqrt{\frac{D}{\pi}}, \quad (15)$$

where  $S^{up}$  is the slope of the linear regression formed by the concentration points in the upper tube. If the slope formed by the concentration points in the lower tube is taken, then the diffusion coefficient which is obtained is the same. The presence of linearity in Figure 4 also shows that the diffusion front has not reached the ends of the tubes, and therefore the self-similar solution given in (13) is valid.

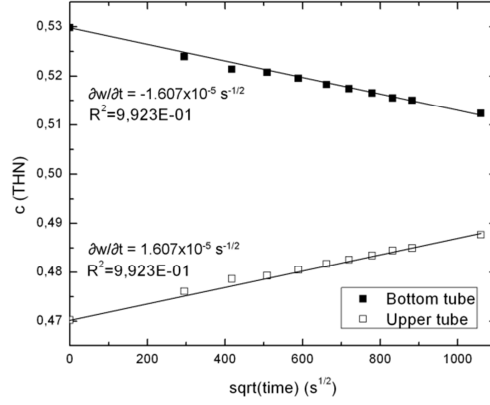


FIG. 4. Variation of the concentration with the square root of time for the mixture THN-IBB at 50% of mass fraction at 25°C.

## 2. New analytical solution for ternary mixtures

In the case of ternary mixtures the procedure is similar to the case of binary mixtures, but it is necessary to use a second change of variable in order to account for the presence of two different eigensolutions of the diffusion matrix, as will be seen. For ternary mixtures Fick's second law may be written as follows:

$$\frac{\partial w_1}{\partial t} = D_{11} \cdot \frac{\partial^2 w_1}{\partial y^2} + D_{12} \cdot \frac{\partial^2 w_2}{\partial y^2}, \quad (16)$$

$$\frac{\partial w_2}{\partial t} = D_{21} \cdot \frac{\partial^2 w_1}{\partial y^2} + D_{22} \cdot \frac{\partial^2 w_2}{\partial y^2}, \quad (17)$$

where  $D_{11}$  and  $D_{22}$  are the diagonal diffusion coefficients and  $D_{12}$  and  $D_{21}$  are the cross-diagonal diffusion coefficients. The variable changes applied in this case are the following:

$$\eta = \frac{y}{2\sqrt{t}}, \quad (18)$$

$$\tau = \sqrt{t}, \quad (19)$$

$$z = \alpha\eta, \quad (20)$$

where  $\alpha$  is an eigenvalue which is to be found. Once more we assume that the diffusion front has not reached the extreme ends of the tubes, and therefore the following self-similar equations are obtained for the concentrations of the components 1 and 2:

$$D_{11}\alpha^2 w_1'' + 2zw_1' + D_{12}\alpha^2 w_2'' = 0, \quad (21)$$

$$D_{21}\alpha^2 w_1'' + D_{22}\alpha^2 w_2'' + 2zw_2' = 0, \quad (22)$$

where primes now denote derivatives with respect to the variable  $z$ .

The boundary conditions in this case are similar to the ones in the case of binary mixtures:

$$\begin{aligned} w_1 &\rightarrow w_{i1}^{bot} \text{ and } w_2 \rightarrow w_{i2}^{bot} \text{ as } \eta \rightarrow -\infty, \\ w_1 &\rightarrow w_{i1}^{up} \text{ and } w_2 \rightarrow w_{i2}^{up} \text{ as } \eta \rightarrow +\infty, \end{aligned} \quad (23)$$

where  $w_{i1}^{up}$ ,  $w_{i1}^{bot}$ ,  $w_{i2}^{up}$  and  $w_{i2}^{bot}$  are the initial conditions of the components 1 and 2 in the upper and lower tubes respectively.

Upon solving the equations (21) and (22) the following expressions are obtained for the concentrations of the two components.

$$w_1 = A \operatorname{erfc}(z_1) + B \operatorname{erfc}(z_2) + w_{i1}^{up}, \quad (24)$$

$$\begin{aligned} w_2 = A \left( \frac{1-D_{11}\alpha_1^2}{D_{12}\alpha_1^2} \right) \operatorname{erfc}(z_1) \\ + B \left( \frac{1-D_{11}\alpha_2^2}{D_{12}\alpha_2^2} \right) \operatorname{erfc}(z_2) + w_{i2}^{up}, \end{aligned} \quad (25)$$

where the constants  $A$  and  $B$  are given by the following functions of the diffusion coefficients and the initial concentrations of the components 1 and 2 in the upper and the lower tubes:

$$A = \frac{D_{12}\alpha_1^2\alpha_2^2(w_{i2}^{bot}-w_{i2}^{up})-\alpha_1^2(w_{i1}^{bot}-w_{i1}^{up})(1-D_{11}\alpha_2^2)}{2(\alpha_2^2-\alpha_1^2)}, \quad (26)$$

$$B = \frac{D_{12}\alpha_1^2\alpha_2^2(w_{i2}^{bot}-w_{i2}^{up})-\alpha_2^2(w_{i1}^{bot}-w_{i1}^{up})(1-D_{11}\alpha_1^2)}{2(\alpha_1^2-\alpha_2^2)}, \quad (27)$$

the values  $\alpha_1$  and  $\alpha_2$ , which are proportional to the eigenvalues of the diffusivity matrix, are given by:

$$\alpha_1 = \sqrt{\frac{-(D_{11}+D_{22})-\sqrt{(D_{11}+D_{22})^2+4(D_{12}D_{21}-D_{11}D_{22})}}{2(D_{12}D_{21}-D_{11}D_{22})}}, \quad (28)$$

$$\alpha_2 = \sqrt{\frac{-(D_{11}+D_{22})+\sqrt{(D_{11}+D_{22})^2+4(D_{12}D_{21}-D_{11}D_{22})}}{2(D_{12}D_{21}-D_{11}D_{22})}}, \quad (29)$$

and

$$z_1 = \alpha_1 \eta, \quad (30)$$

$$z_2 = \alpha_2 \eta. \quad (31)$$

As in the case of binary mixtures, the expressions given in Eqs. (24) and (25) are integrated and then divided by the length of each tube to give the mean concentration for each component in each of the tubes.

$$\frac{1}{L} \int_0^L w_1 dy = w_{i1}^{up} + \frac{2}{L} \sqrt{\frac{t}{\pi}} \left( \frac{A}{\alpha_1} + \frac{B}{\alpha_2} \right), \quad (32)$$

$$\begin{aligned} \frac{1}{L} \int_0^L w_2 dy \\ = w_{i2}^{up} + \frac{2}{L} \sqrt{\frac{t}{\pi}} \left( \frac{A}{\alpha_1} \left( \frac{1-D_{11}\alpha_1^2}{D_{12}\alpha_1^2} \right) + \frac{B}{\alpha_2} \left( \frac{1-D_{11}\alpha_2^2}{D_{12}\alpha_2^2} \right) \right). \end{aligned} \quad (33)$$

Equations (32) and (33) show that, in the case of ternary mixtures, the concentration of each component also varies linearly with the square root of time. Equations (32) and (33) may be therefore manipulated as before to give the slope of the line corresponding to each component:

$$S_1 = \frac{2}{L\sqrt{\pi}} \left( \frac{A}{\alpha_1} + \frac{B}{\alpha_2} \right), \quad (34)$$

$$S_2 = \frac{2}{L\sqrt{\pi}} \left( \frac{A}{\alpha_1} \left( \frac{1-D_{11}\alpha_1^2}{D_{12}\alpha_1^2} \right) + \frac{B}{\alpha_2} \left( \frac{1-D_{11}\alpha_2^2}{D_{12}\alpha_2^2} \right) \right), \quad (35)$$

where  $S_1$  and  $S_2$  are the slopes formed by the linear regression of the concentration of components 1 and 2 respectively, with respect to the square root of time.

In order to determine the molecular diffusion coefficients in ternary mixtures, it is necessary to have experimental data from two independent experiments of the same mixture where the initial concentrations are different. In this way, a system of four equations (i.e. Eqs. (34) and (35) for two different experiments) and four unknowns (the four diffusion coefficients) is obtained. It is impossible to solve for the four coefficients analytically because the four equations are highly nonlinear, but they may be found very rapidly using a straightforward four-dimensional Newton-Raphson method.

### III. RESULTS AND DISCUSSION

In this section, first the molecular diffusion coefficients in binary mixtures determined by the classical and new analytical solutions are shown and compared, and then, the diagonal and cross-

diagonal molecular diffusion coefficients in ternary mixtures are determined from the new analytical solution.

### A. Binary mixtures

In previous works (Refs. 19-21) the validity of the SST technique and the classical analytical solution (given by Eqs. (4) and (5)) for the determination of the molecular diffusion coefficients in binary mixtures have been shown to be accurate. Figure 5 compares the results obtained by the present new formulation (given by Eq. (15)) with the ones obtained by the classical solution (given by Eqs. (4) and (5)). The data used are for the binary mixtures formed by THN, IBB and *n*C12 with 50% of mass fraction and at 25°C, and for the mixture water-isopropanol for many different mass concentrations of water and at 25°C.

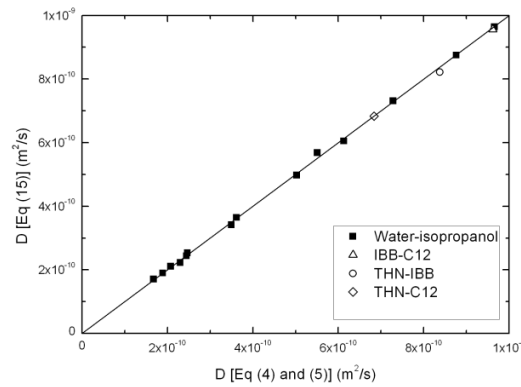


FIG. 5. Comparison of the results obtained by the equations (4) and (5), and the equation (15) for the binary mixtures formed by THN, IBB and *n*C12 with 50% of mass fraction and the mixture formed by water-isopropanol for many different mass concentrations of water; all cases are at 25°C.

The very good agreement between the results obtained by the two methods demonstrates the validity of the new analytical solution developed in this work, for the case of binary mixtures.

### B. Ternary mixtures

In Larrañaga *et al.*<sup>15</sup> the determination of the diagonal and cross-diagonal molecular diffusion coefficients using the classical analytical solution (Eqs. (6) and (7)) was attempted. However, as has been pointed out, the establishment of a fitting method which allows reproducible results to be obtained and which does not depend on the fitting conditions was found to be impossible. By contrast, the new analytical solution developed in this work only requires a simple straight-line

fit to obtain slopes and then the diffusion coefficients in ternary mixtures may be calculated directly by the Newton-Raphson method.

In this work the results obtained for the ternary mixture THN-IBB-*n*C12 with equal mass fractions and at 25°C are shown, and they are compared to the results published in the literature.

The experimental determination of the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures requires experimental data from two independent experiments where the initial concentrations are different. Table I shows the initial concentrations of each component in the two experiments used in this case.

TABLE I. Initial concentrations and slopes,  $S$  ( $s^{-1/2}$ ), for each component in the upper and the bottom tubes, in the two experiments carried out in this work, at 25°C.

	Exp. 1	Exp. 2
w (THN) up	0.3033	0.3033
w (THN) bot	0.3633	0.3633
w (IBB) up	0.3433	0.3333
w (IBB) bot	0.3233	0.3333
w (C12) up	0.3533	0.3633
w (C12) bot	0.3133	0.3033
$S$ (THN) up ( $s^{-1/2}$ )	$1.58 \times 10^{-5}$	$1.49 \times 10^{-5}$
$S$ (THN) bot ( $s^{-1/2}$ )	$-1.58 \times 10^{-5}$	$-1.49 \times 10^{-5}$
$S$ (C12) up ( $s^{-1/2}$ )	$-0.96 \times 10^{-6}$	$-1.43 \times 10^{-5}$
$S$ (C12) bot ( $s^{-1/2}$ )	$0.96 \times 10^{-6}$	$1.43 \times 10^{-5}$

As for the case of binary mixtures, the variation of the concentration with the square root of time is linear. Figure 6 shows some experimental results for the mixture THN-IBB-*n*C12 with equal mass fraction and 25°C, corresponding to the experiment 1 of the Table I.

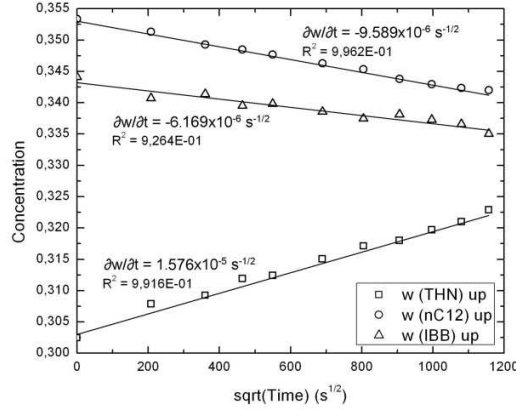


FIG. 6. Variation of the concentration with the square root of time for the components THN, IBB and *n*C12 at 25°C, obtained from the upper tube of the SST technique.

Prior to showing further results, it is necessary to discuss the implications of the choice of the order of components in a ternary mixture. The four molecular diffusion coefficients which are found depend on which two components of the three are assigned to the variables  $w_1$  and  $w_2$  in the flux equations (36) and (37). This is why special care needs to be taken when results from different scientific groups are compared.

$$J_1 = -\rho(D_{11}\nabla w_1 + D_{12}\nabla w_2), \quad (36)$$

$$J_2 = -\rho(D_{21}\nabla w_1 + D_{22}\nabla w_2). \quad (37)$$

However, it is quite straightforward to manipulate the pair of coupled Fick's equations for these two components into the corresponding forms for either of the other two possible choices of the components as shown in Königer *et al*<sup>10</sup>.

Because of the analysis method used in the present laboratory, the best accuracy was obtained when the components with highest and the lowest densities are chosen, and it is these that were generally chosen to be  $w_1$  and  $w_2$ . However, in order to compare the present results with those available in the literature, the molecular diffusion coefficients for all three possible orders of components have been determined experimentally. Table II shows the diagonal and cross-diagonal molecular diffusion coefficients for the three possible orders of components in the mixture.

TABLE II. Molecular diffusion coefficients determined in this work for the mixture THN-IBB-*n*C12 with equal mass fraction and at 25°C for the three possible orders of components.

Order of components $w_1-w_2-w_3$	$D_{11} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{12} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{21} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{22} \times 10^{-10}$ (m <sup>2</sup> /s)
THN-IBB- <i>n</i> C12	6.16	-4.61	0.37	11.40
THN- <i>n</i> C12-IBB	11.30	5.08	0.14	6.65
<i>n</i> C12-IBB-THN	6.54	-0.51	-0.37	11.06

In the three cases the molecular diffusion coefficients satisfy the restrictions detailed in Mutoru *et al.*<sup>24</sup>.

The literature about molecular diffusion in ternary mixtures of hydrocarbons is very limited. For our same mixture and composition, there are only three works published. Königer *et al.*<sup>10</sup> determined the molecular diffusion coefficients using the two colour optical beam deflection technique (OBD), considering the component order *n*C12-IBB-THN. Mialdun *et al.*<sup>11</sup> measured the molecular diffusion coefficients by a counter flow cell fitted with an optical interferometry device (CFC), and the component order THN-IBB-*n*C12 was preferred. Afterwards, this same team published a new work (Ref. 16) where two independent techniques were used: the counter flow cell fitted with an optical interferometry device (CFC) and Taylor dispersion technique (TDT). This last work (Ref. 16) emerges as more confident for the team of Mialdun *et al.*; however, as the published results for molecular diffusion coefficients in ternary mixtures are limited, we have compared the results of the three works available in the literature.

Table III shows the eigenvalues of the diffusion matrix determined here by the SST technique (rows 2, 3 and 4) and the ones determined by OBD (Ref. 10) (row 5), CFC (Ref. 11) (row 6), TDT (Ref. 16) and CFC (Ref. 16) (rows 7 and 8). The second column indicates the order in which the components have been taken in each case. The eigenvalues of the diffusion matrix do not depend on the order of the components chosen, so they may be compared directly.

TABLE III. Comparison between the eigenvalues of the diffusion matrix obtained in this work and the results of the literature.

Data source	Order of components $w_1-w_2-w_3$	$\widehat{D}_1 \times 10^{-10}$ (m <sup>2</sup> /s)	$\widehat{D}_2 \times 10^{-10}$ (m <sup>2</sup> /s)
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	THN-IBB- <i>n</i> C12	6.51	11.10
Present study: SST	THN- <i>n</i> C12-IBB	6.49	11.50
	<i>n</i> C12-IBB-THN	6.50	11.11
OBD <sup>10</sup>	<i>n</i> C12-IBB-THN	6.81	10.99
CFC <sup>11</sup>	THN-IBB- <i>n</i> C12	7.26	11.23
TDT <sup>16</sup>	THN-IBB- <i>n</i> C12	6.82	9.9
CFC <sup>16</sup>	THN-IBB- <i>n</i> C12	7.09	11.17

As can be observed, the agreement between the determined eigenvalues is reasonable, obtaining variations between 1% and 12%.

In order to make a comparison between the molecular diffusion coefficients obtained in this work and the ones published in the literature, in the three possible cases of order of components, the transformation of the diffusion matrix detailed in the Eqs. (A8)-(A11) of Königer *et al.*<sup>10</sup> has been applied to the results of this work and to the results of the literature, for the cases needed. Table IV shows the results found when the order of components is THN-IBB-*n*C12. Table V shows the results obtained when the order of components considered is *n*C12-IBB-THN. Finally, Table VI shows the results obtained in the case of considering the order of components THN-*n*C12-IBB.

TABLE IV. Comparison of the diffusion coefficients for the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25°C, where THN and IBB form components  $w_1$  and  $w_2$  respectively.

Data source	Order of components $w_1-w_2-w_3$	$D_{11} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{12} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{21} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{22} \times 10^{-10}$ (m <sup>2</sup> /s)
Present study: SST		6.16	-4.61	0.37	11.40
Present study: SST*		6.22	-5.08	0.28	11.73
OBD <sup>10*</sup>	THN-IBB- <i>n</i> C12	5.62	-5.91	1.08	12.18
CFC <sup>11</sup>		6.92	1.06	-1.37	11.57
TDT <sup>16</sup>		10.31	0.33	-4.36	6.41
CFC <sup>16</sup>		11.61	0.32	-6.18	6.65

\* Data has been transformed for the same order of components (Eqs. (A8)-(A11) in Königer *et al.*<sup>10</sup>).

TABLE V. Comparison of the diffusion coefficients in the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25°C, where *n*C12 and IBB form components  $w_1$  and  $w_2$  respectively.

Data source	Order of components $w_1-w_2-w_3$	$D_{11} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{12} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{21} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{22} \times 10^{-10}$ (m <sup>2</sup> /s)
Present study: SST	<i>n</i> C12-IBB-THN	6.54	-0.51	-0.37	11.06
Present study: SST*		6.51	-0.14	-0.28	11.14
OBD <sup>10</sup>		6.70	0.43	-1.08	11.10
CFC <sup>11*</sup>		5.55	-7.08	1.37	12.94
TDT <sup>16*</sup>		5.95	-0.79	4.36	10.77
CFC <sup>16*</sup>		5.43	-1.54	6.18	12.83

\* Data has been transformed for the same order of components (Eqs. (A8)-(A11) in Königer *et al.*<sup>10</sup>).

TABLE VI. Comparison of the diffusion coefficients in the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25°C, where THN and *n*C12 form components  $w_1$  and  $w_2$  respectively.

Data source	Order of components $w_1-w_2-w_3$	$D_{11} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{12} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{21} \times 10^{-10}$ (m <sup>2</sup> /s)	$D_{22} \times 10^{-10}$ (m <sup>2</sup> /s)
Present study: SST	THN- <i>n</i> C12-IBB	11.30	5.08	0.14	6.65
OBD <sup>10*</sup>		11.53	5.91	-0.43	6.27
CFC <sup>11*</sup>		5.86	-1.06	7.08	12.63
TDT <sup>16*</sup>		9.98	-0.33	0.79	6.74
CFC <sup>16*</sup>		11.28	-0.32	1.55	6.97

\* Data has been transformed for the same order of components (Eqs. (A8)-(A11) in Königer *et al.*<sup>10</sup>).

As may be seen in Tables IV-VI, the agreement between the diagonal diffusion coefficients determined in this work and the ones published in the literature is reasonable in most of the cases, especially with the results shown in Königer *et al.*<sup>10</sup>. In the case of the cross-diagonal diffusion coefficients the differences are bigger, appearing in some cases even a disagreement in the sign. The disagreements between the results of the different teams show the difficulty of the determination of the molecular diffusion coefficient in ternary mixtures. It is necessary to continue working in order to optimize the experimental techniques and the corresponding

analysis methods. For that purpose, we plan to continue analyzing this mixture but in the whole range of concentrations.

In addition to the comparison of the molecular diffusion coefficients, it is also possible to compare the Soret coefficients of the mixture studied in this work. The Soret coefficient can be determined from the measurements of the thermodiffusion and the molecular diffusion coefficients, by the expression shown in Mialdun and Shevtsova<sup>17</sup> In Blanco *et al.*<sup>25</sup> this scientific team published the thermodiffusion coefficients for the mixture studied in this work determined by the thermogravitational technique (TGC). The molecular diffusion coefficients determined in this work by the SST technique allow determining Soret coefficients for the mixture THN-IBB-*n*C12 with equal mass fraction, at 25°C. Table VII shows the results obtained in this work for the three different cases of order of components (rows 2-4) and the results determined experimentally by the OBD technique (Ref. 10) (row 5).

TABLE VII. Comparison of the Soret coefficients in the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25°C

Data source	Order of components $w_1-w_2-w_3$	$S_T^{THN} \times 10^{-3}$ $K^{-1}$	$S_T^{IBB} \times 10^{-3}$ $K^{-1}$	$S_T^{nC12} \times 10^{-3}$ $K^{-1}$
	THN-IBB- <i>n</i> C12	1.83	0.05	-1.88
Present study: TGC + SST	THN- <i>n</i> C12-IBB	1.82	0.07	-1.89
	<i>n</i> C12-IBB-THN	1.83	0.05	-1.88
OBD <sup>10</sup>	<i>n</i> C12-IBB-THN	2.11	-0.96	-1.15

As may be observed, independently of the order of components chosen, the Soret coefficient corresponding to each coefficient is the same (rows 2-5 of Table VII). The agreement between the results obtained in this work and the ones shown in Königer *et al.*<sup>10</sup> is optimistic in order to continue developing the techniques to determine the transport properties in multicomponent mixtures, taking into account the limited experimental results available for ternary mixtures.

#### IV. CONCLUSIONS

An analytical method based upon the notion of self-similarity has been developed to enable the determination of molecular diffusion coefficients in ternary mixtures by the SST technique. This method, when combined with a four-dimensional Newton-Raphson scheme, yields the diffusion coefficients very rapidly. The accuracy of these coefficients depends firstly on the diffusion front not having yet reached the extreme ends of the tubes in our SST experiment, and secondly on the accuracy of the experimental technique itself. We would claim that both of these conditions are satisfied because the data shown in Figures 4 and 6 yield lines which are almost exactly linear.

In this work all the diagonal and cross-diagonal molecular diffusion coefficients corresponding to the mixture THN-IBB-*n*C12 with equal mass fraction and at 25°C have been determined. After comparing these values with the ones shown in the literature, the agreement between the eigenvalues of the diffusion matrix is particularly good and the agreement between the molecular diffusion coefficients is acceptable, especially in the case of the diagonal diffusion coefficients. As can be observed, the cross-diagonal molecular diffusion coefficients are much more sensitive.

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#### REFERENCES

- <sup>1</sup>F. Capuano, L. Paduano, G. D’Errico, G. Mangiapia, R. Sartorio, *Phys. Chem. Chem. Phys.*, **13**, 3319-3327 (2011).
- <sup>2</sup>T. Takahashi, Y. Minamino, *J. Alloys and Compounds*, **545**, 168 – 175 (2012).

- <sup>3</sup>H. Tello Alonso, A. C. Rubiolo, S. E. Zorrilla, J. Food Engin., **109**, 490-495 (2011).
- <sup>4</sup>A. Fick, Annalen der Physik, **94**, 59-86 (1855).
- <sup>5</sup>P. Blanco, P. Polyakov, M. M. Bou-Ali, S. Wiegand, J. Phys. Chem. B, **112** 8340 – 8345 (2008).
- <sup>6</sup>J. F. Dutrieux, J. K. Platten, G. Chavepeyer, M. M. Bou-Ali, J. Phys. Chem. B, **106** 6104-6114 (2002).
- <sup>7</sup>M. Gebhardt, W. Köhler, A. Mialdun, V. Yasnou, V. Shevtsova, J. Chem. Phys., **138**, 114503 (2013).
- <sup>8</sup>A. A. Alizadeh, W. A. Wakeham, Int. J. Thermophys., **3**, 307 (1982).
- <sup>9</sup>P. Blanco, M. M. Bou-Ali, P. Urteaga, Patente ES 2351822 (A1) (2011).
- <sup>10</sup>A. Königer, H. Wunderlich, W. Köhler, J. Chem. Phys., **132**, 174506 (2010).
- <sup>11</sup>A. Mialdun, V. Yasnou, V. Shevtsova, C. R. Mecanique, **341**, 462-468 (2013).
- <sup>12</sup>A. Leahy-Dios, M. M. Bou-Ali, J. K. Platten A. Firoozabadi, J. Chem. Phys., **122**, 234502.1-234502.12 (2005).
- <sup>13</sup>C. I. Santos, M. A. Estes, V. M. Lobo, A. C. Ribeiro, J. Chem. Thermodynamics, **59**, 139 – 143 (2013).
- <sup>14</sup>X. Liu, A. Martin-Calvo, E. McGarrity, S. K. Schnell, S. Calero, J-M Simon, D. Bedeaux, S. Kjelstrup, A. Bardow, T. J. H. Vlugt, Industrial and Engineering Chemistry Research, **51**, 10247 – 10258 (2012).
- <sup>15</sup>M. Larrañaga, M.M. Bou-Ali, D. Soler, M. Martinez-Agirre, A. Mialdun V. Shevtsova, C. R. Mecanique, **341**, 356-364 (2013).
- <sup>16</sup>A. Mialdun, V. Sechenyh J. C. Legros, J.M. Ortiz de Zárate, V. Shevtsova, J. Chem. Phys., **139**, 104903 (2013).

- <sup>17</sup>A. Mialdun, V. Shevtsova, J. Chem. Phys., **138**, 161102 (2013).
- <sup>18</sup>Diffusion Coefficient Measurements in ternary Mixtures DCMIX-NCR-00022-QS.
- <sup>19</sup>D. Alonso de Mezquia, M. M. Bou-Ali, M. Larrañaga, J. A. Madariaga, C. Santamaría, J. Phys. Chem. B, **116** 2814-2819 (2012).
- <sup>20</sup>D. Alonso de Mezquia, F. Doumenc, M. M. Bou-Ali, J. Chemical and Engineering Data, **57**, 776-783 (2012).
- <sup>21</sup>A. Mialdun, V. Yasnou V. Shevtsova, A. Königer, W. Köhler, D. Alonso de Mezquia, M. M. Bou-Ali, J. Chem. Phys., **136** 244512 (2012).
- <sup>22</sup>M.J. Sawicka, J. A. Soroka Cent. Eur. J. Chem., **11(7)**, 1239-1247 (2013).
- <sup>23</sup>H. S. Carslaw, J.C. Jaeger, *Conduction of Heat in Solids* (Oxford at the Clarendon press, 1959) p.50.
- <sup>24</sup>J.W. Mutoru, A. Firoozabadi, J. Chem. Therm., **43** 1192-1203 (2011).
- <sup>25</sup>P. Blanco, M. M. Bou-Ali, J. K. Platten, D. Alonso de Mezquia, J. A. Madariaga C. Santamaría, J. Chem. Phys., **132** 114506 (2010).

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